A NETWORK THERMODYNAMIC MODEL FOR TRANSIENT EFFECTS IN ELECTROKINETIC ENERGY CONVERSION

Carlos F. GONZÁLEZ-FERNÁNDEZ[a], José HORNO[b] and Fernando GONZÁLEZ-CABALLERO[a]

[a] *Department of Applied Physics, University of Granada, E-18071 Granada, Spain and*
[b] *Department of Applied Physics, University College of Jaén, E-23071 Jaén, Spain*

Received September 27, 1988
Accepted December 15, 1988

A network model is proposed allowing the transient effects in electrokinetic phenomena to be studied in terms of the network thermodynamics concept. Relaxation times for the build-up of electroosmotic pressure and streaming potential, time required for the electrokinetic energy conversion to reach its maximum efficiency and the optimum outforce for the energy conversion are readily obtained by this method.

Electrokinetic phenomena involve conversion of mechanical energy into electrical energy and vice versa. The efficiency of the energy conversion has been studied on both the theoretical[1,2] and experimental[3,4] levels, and its dependence on the properties of the system have been analyzed[5]. The above studies are based on the thermodynamics of irreversible processes, where the efficiency of energy conversion is regarded as the ratio of the output flow and force to the input flow and force. Kedem and Caplan[2] gave explicit expressions for the conditions of the maximum efficiency within the scope of Onsager's thermodynamics. More recently, Peusner[6] extended this concept to the non-reciprocal linear range using network thermodynamics theory[7-9]. The network approach enables a thermodynamic system to be described by a graphical representation analogous to circuit diagrams in electrical network theory.

Transient processes in the two electrokinetic phenomena, viz. electroosmotic pressure and streaming potential, have been analyzed by several authors[3,10-12]. While the efficiency of energy conversion in these processes is zero in the initial state ($t = 0$) and in the stationary state ($t \to \infty$), between these limiting states it is nonzero. Thus, important parameters of the processes are the time the efficiency of energy conversion reaches its maximum and the corresponding value of the output quantity. These can be determined in a simple and general way by using network thermodynamics methods.

In this paper, a linear energy converting two-port is set up allowing transient effects to be included in the study of the dynamics of electrokinetic phenomena.

THEORETICAL

In the linear range, the electrokinetic phenomena are described by phenomenological equations which, in conductance terms, can be written as

$$J_1 = L_{11}X_1 + L_{12}X_2 \,,$$
$$J_2 = L_{21}X_1 + L_{22}X_2 \,, \qquad (1)$$

where J_i and X_j are thermodynamic flows and forces, respectively, and L_{ij} are phenomenological coefficients, assumed in this treatment to be constant. Classical electrical network theory shows that for reciprocal systems ($L_{12} = L_{21}$), Eqs (*1*) can be represented by a passive Π-network model (two-port), involving three conductances, viz. $L_{11} - L_{12}$, L_{12}, and $L_{22} - L_{12}$, and no current or voltage sources. The relaxation in the transient processes then can be accounted for by including a capacitor in this model. For the situation where the input force X_1 is maintained constant, the model so obtained is shown in Fig. 1*a*.

The efficiency of energy conversion, η, can be described by the equation

$$\eta = (-X_o J_o)/(X_i J_i) = (-X_2 J_2)/(X_1 J_1) \,, \qquad (2)$$

where the subscripts o and i refer to the output and input quantities respectively and the negative sign is related with the opposite directions of the input and output

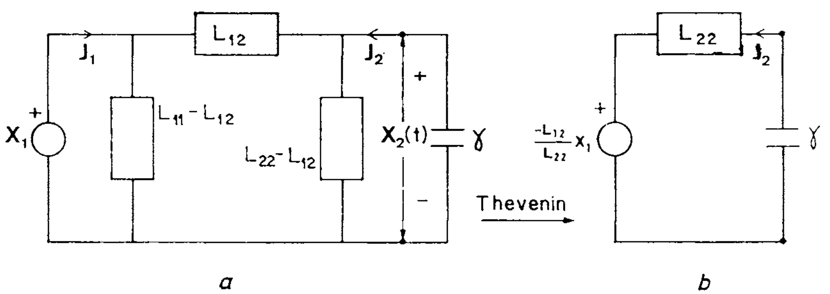

FIG. 1

a Network model of transient effects in electrokinetic phenomena: X_1 = constant. *b* Thevenin's model. Symbols are given in the text signals. Using Eqs (*1*), η can be written as

$$\eta = - \frac{X_2^2 + (L_{12}/L_{22}) X_1 X_2}{(L_{12}/L_{22}) X_1 X_2 + (L_{11}/L_{22}) X_1^2} \,. \qquad (3)$$

The network shown in Fig. 1*a* can be readily analyzed by using the Thevenin theorem (Fig. 1*b*). From this model we obtain directly

$$(\gamma/L_{22})(X_2/\mathrm{d}t) = -(L_{12}/L_{22}) X_1 - X_2 \qquad (4)$$

which integrated for the initial condition $X_2 = 0$ $(t = 0)$ gives

$$X_2 = -(L_{12}/L_{22}) X_1 [1 - \exp(-t/\tau)] \,, \qquad (5)$$

where the relaxation time τ is given by

$$\tau = \gamma/L_{22} \,. \qquad (6)$$

In the stationary state $(t \to \infty)$, force X_2 takes the value

$$X_2(\infty) = -(L_{12}/L_{22}) X_1 \,. \qquad (7)$$

By inserting Eq. (*7*) in Eq. (*3*), the efficiency is obtained in the form

$$\eta = \frac{X_2[X_2(\infty) - X_2]}{X_2(\infty)[X_2(\infty) q^{-2} - X_2]} \,, \qquad (8)$$

where $q = L_{12}(L_{11}L_{22})^{-1/2}$ is the well-known degree of coupling, which serves as an indicator of the energy conversion process.

The maximum efficiency can be found from the condition

$$\partial\eta/\partial X_2 = 0 \,, \qquad (9)$$

wherefrom the optimum outforce (X_2) for energy conversion is

$$(X_2)_{\max} = X_2(\infty)/[1 + (1 - q^2)^{1/2}] \,. \qquad (10)$$

By substituting in Eq. (*8*) we obtain an expression for the maximum efficiency that is identical with the result obtained by Kedem and Caplan[2]. Furthermore, Eq. (*10*) reveals that if the coupling is small $(q \ll 1)$, η attains its maximum when the output force assumes half of its stationary state value; this agrees with the experimental result obtained by Blokhra and coworkers[3].

The time required for attaining the maximum efficiency of energy conversion can be calculated by inserting Eqs (7) and (10) in Eq. (5), which gives

$$t = \tau \ln \left[1 + (1 - q^2)^{1/2}\right] / \left[(1 - q^2)^{1/2}\right] ; \qquad (11)$$

if the coupling is small ($q \ll 1$), then

$$t = \tau \ln 2 . \qquad (12)$$

For cases where the process meets the condition that X_2 is constant, the above expressions can be obtained in a straightforward way. It is only necessary to change the subscripts 1 and 2 of the phenomenological variables and coefficients.

To obtain values of the capacitance γ in the network model, we only have to take into account the constitutive law of a capacitor, viz.

$$J = \gamma(\mathrm{d}X/\mathrm{d}t) . \qquad (13)$$

Thus, when identifying J_1 and J_2 with the volume flow and electrical current, and X_1 and X_2 with the pressure and electrical potential differences, respectively, the current in a streaming potential process (X_1 is constant) is given by

$$J_2 = \mathrm{d}Q/\mathrm{d}t = C(\mathrm{d}X_2/\mathrm{d}t) , \qquad (14)$$

where Q and C are the electrical charge and capacitance, respectively. Comparison of Eqs (13) and (14) shows that γ is equal to the electrical capacitance of the system. Similarly, the volume flow for the case where X_2 is constant can be written as

$$J_1 = s(\mathrm{d}h/\mathrm{d}t) = (s/\varrho \boldsymbol{g}) \left[\mathrm{d}(\varrho \boldsymbol{g} h)/\mathrm{d}t\right] = (s/\varrho \boldsymbol{g}) (\mathrm{d}X_1/\mathrm{d}t) , \qquad (15)$$

where s is the cross-section of the capillary tube in which the liquid rises to the height h during the electroosmotic flow, ϱ is the density of the liquid and $\boldsymbol{g}$ is the gravitational acceleration. The capacitance of electroosmosis is obtained by comparison of Eqs (13) and (15).

In conclusion, analysis of a conveniently set-up two-port allows transient effect in electrokinetic phenomena to be studied by network thermodynamics methods. In particular, this approach enables the relaxation times for the build-up of the electroosmotic pressure and streaming potential as well as the time in which the maximum efficiency of the electrokinetic energy conversion is reached, along with the optimum outforce, to be easily obtained.

REFERENCES

1. Osterle J. F.: Appl. Mech. *31*, 161 (1964).
2. Kedem O., Caplan S. R.: Trans. Faraday Soc. *61*, 1897 (1965).
3. Blokhra R. L., Agarwall S. K., Arora N.: Colloid Interface Sci. *73*, 88 (1980).
4. Srivastava R. C., Abraham M. G.: Trans. Faraday Soc. *72*, 2631 (1976).
5. Hidalgo-Alvarez R., González-Caballero F., Pardo G.: Phys. Lett. A *94*, 325 (1983).
6. Peusner L.: Theor. Biol. *102*, 7 (1983).
7. Peusner L.: *Thesis*. Harvard University, Harvard 1970. Reprinted by Entropy, Ltd., Lincoln, MA 1987.
8. Peusner L.: *Studies in Network Thermodynamics*. Elsevier, Amsterdam 1986.
9. Mikulecky D. C., Wiegand W. A., Shiner J. S.: J. Theor. Biol. *69*, 471 (1977).
10. Haase R.: Z. Phys. Chem. (Wiesbaden) *103*, 235 (1976).
11. Srivastava R. C., Jain A. K.: J. Hydrol. *25*, 339 (1975).
12. Kumar R., Singh K.: Indian J. Chem., A *19*, 511 (1980).

Translation revised by P. Adámek.